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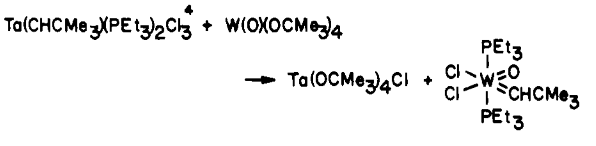
(22) For a description of the importance and role of molecular deformation in chemical reactivities, see also ref 10.
(23) We have also performed calculations on the anionic additive reactions. In contrast to ref 21, we use diffuse functions on hydrogen and carbon and find, in the Hartree–Fock (HF) approximation, barrier heights of 17.4 and 20.0 kcal/mol for the addition of H^- to C_2H_2 and C_2H_4, respectively. These results are much larger than the HF values of 3.2 and 1.9 kcal/mol reported in ref 21, but rather close to their 3 × 3 CI values of 16.7 and 16.6 kcal/mol. For a more complete study of the $H^- + C_2H_2$ reaction, cf. C. E. Dykstra, A. J. Arduengo, and T. Fukumaga, *J. Am. Chem. Soc.*, **100**, 6007 (1979).
(24) For an ab initio rate study of the $H + C_2H_4$ reaction, cf. S. Nagase, T. Fueno, and K. Morokuma, *J. Am. Chem. Soc.*, **101**, 5849 (1979).

Communications to the Editor

Tungsten–Oxo Alkylidene Complexes as Olefin Metathesis Catalysts and the Crystal Structure of $W(O)(CHCMe_3)(PEt_3)Cl_2$[1]

Sir:

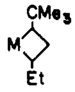
For some time we have been trying to prepare molybdenum- or tungsten-alkylidene complexes which are isoelectronic with known niobium or tantalum alkylidene complexes.[2a] Since a direct approach so far has yielded only one, rather esoteric type,[2b] we turned to indirect routes. The first successful reaction of this type is shown in eq 1.[3] Analogous benzylidene (**1b**), ethylidene (**1c**), propylidene (**1d**), and methylene (**1e**) complexes were prepared by treating **1a** with $RCH{=}CH_2$ (R = Ph, Me, Et, H) in the presence of a trace of $AlCl_3$.[5] We report here that these oxo alkylidene complexes are catalysts for the metathesis of terminal and internal olefins and describe the isolation and crystal structure of a *five*-coordinate, active metathesis catalyst, $W(O)(CHCMe_3)(PEt_3)Cl_2$.



1a

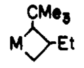
(1)

$W(O)(CHCMe_3)(PEt_3)_2Cl_2$ in benzene in the presence of ~0.5 equiv of $AlCl_3$[6] in 1–2 h reacts with 1-butene to give 3,3-dimethyl-1-butene (0.95+ equiv), but no 2,2-dimethyl-3-hexenes (the other possible type of metathesis product) or olefin products of β elimination from a metallacyclobutane intermediate.[7] The solution also contains 1–2 equiv of 3-hexene(s) (geometry undetermined) and some ethylene (most is in the gas phase). The solution was filtered at this point and the contents were examined by ^1H, ^{13}C, and ^{31}P NMR in C_6D_6. We showed an organometallic product of type **1** to be present in ~55% yield (by ^1H NMR integration vs a toluene standard); it was a mixture of **1d** (~80%) *and* **1e** (~20%).[8] Since 3,3-dimethyl-1-butene is the only product of the initial reaction between **1a** and 1-butene, **1e** must form in a subsequent reaction of **1d** with 1-butene. This suggests that formation and metathesis of **2a** is faster than formation and metathesis of **3a**. Presumably, the same is true of **2b** vs. **3b**.[9]

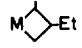


2a

2b



3a



3b

A reaction identical with the above continues to produce ethylene (which is vented every few hours) and 3-hexenes. After 24 h ~17 equiv of 3-hexenes are found.

$W(O)(CHCMe_3)(PEt_3)_2Cl_2$ in chlorobenzene in the presence of ~0.5 equiv of $AlCl_3$ reacts with *cis*-2-pentene to give the two initial metathesis products shown in eq 2 in 2 h, **1c** and **1d** in a ratio of ~1:1, and 2-butenes (~70% trans) and 3-hexenes steadily over the next 24 h. The total number of turnovers in 24 h is ~50.

$$\mathbf{1a} + cis\text{-}MeCH{=}CHEt \xrightarrow{2\ h} (0.22)\,trans\text{-}Me_3CCH{=}CHMe_3 + (0.13)\ trans\text{-}MeCCH{=}CHEt + \mathbf{1c} + \mathbf{1d} \quad (2)$$

The metathesis reactions (especially of 2-pentene) proceed more slowly in benzene than they do in chlorobenzene. If $AlEtCl_2$ is used instead of $AlCl_3$, 1-hexene is metathesized at about the same rate for the first 12 h (as is observed with $AlCl_3$), but then 2-butene forms (probably via a nonmetathesis related isomerization pathway) and all possible metathesis products are produced. Other Lewis acids such as $TaCl_5$, $SnCl_2$, $ZrCl_4$, or $SbCl_5$ also are successful cocatalysts. In all reactions the catalytic activity slows considerably with time and eventually no oxo alkylidene complexes of type **1** can be recovered from or observed in the mixture.

In other studies[10] we postulate that an octahedral coordination site must be present on tantalum for an olefin to react with the alkylidene ligand. The following results suggest that this is true here as well. Halides exchange readily between W and Al; when 1 equiv of $AlBr_3$ is added to **1a** in benzene, $W(O)(CHCMe_3)(PEt_3)_2Br_2$ is formed essentially quantitatively in a few minutes, according to the ^{31}P NMR spectrum of the filtered mixture.[11] We also know that, in the absence of a Lewis acid, complexes of type **1** react very slowly with olefins and not at all in the presence of added PEt_3. Unfortunately, these results do not tell us whether loss of halide, loss of PEt_3, or loss of both yields a metathesis catalyst.

We can remove one PEt_3 ligand by adding transition metal complexes which will scavenge phosphine. One of the most successful experiments is shown in eq 3. Interestingly, **4** will metathesize terminal and internal olefins in chlorobenzene

$$\mathbf{1a} + 0.5Pd(PhCN)_2Cl_2 \xrightarrow[\text{toluene}]{3\ h} 0.5Pd(PEt_3)_2Cl_2 + \underset{\mathbf{4}}{W(O)(CHCMe_3)(PEt_3)Cl_2}{}^{12} \quad (3)$$

in the absence of $AlCl_3$ at an initial rate which is at least equal to that of **1** plus $AlCl_3$, but the system is shorter lived. Therefore **4** is at least a plausible active intermediate in the system **1** plus $AlCl_3$.

$W(O)(CHCMe_3)(PEt_3)Cl_2$ crystallizes in the centrosymmetric orthorhombic space group *Pbca* with $a = 9.111\ (2)$, $b = 15.709\ (4)$, $c = 24.207\ (6)$ Å; $V = 3465\ (1)$ Å^3 and ρ(calcd) = 1.76 g cm^{-3} for mol wt 459.0; and $Z = 8$. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer using a coupled θ(crystal)–2θ(counter) scan technique[13] and graphite-monochromatized Mo Kα radiation. Data were corrected for absorption ($\mu = 74.3\ cm^{-1}$) and the structure was solved by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. All nonhydrogen atoms were located. The tungsten atom lies in a pseudo special position (~1/2, ~1/2, ~1/8) and

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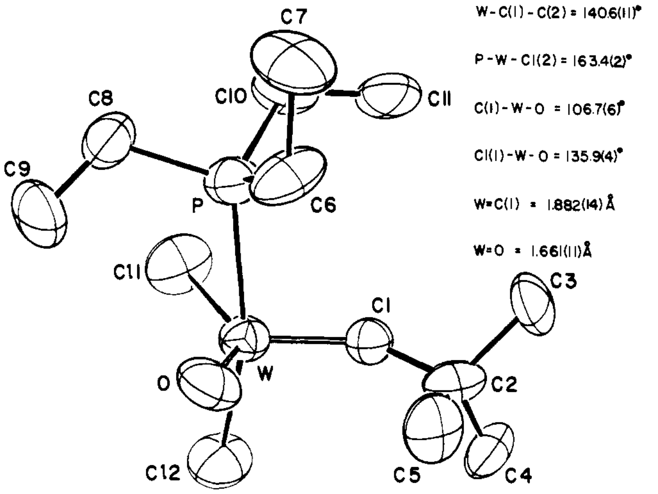

Figure 1. ORTEP drawing of the structure of $W(O)(CHCMe_3)(PEt_3)Cl_2$ showing all nonhydrogen atoms.

half of the data is systematically weak. Discrepancy indices are $R_F = 0.147$ and $R_{wF} = 0.068$ for all 3055 reflections and $R_F = 0.082$ and $R_{wF} = 0.060$ for those 1769 reflections with $|F_{obsd}| > 3\sigma[|F_{obsd}|]$.

The molecular geometry is shown in Figure 1. The molecule is a distorted trigonal bipyramid in which the oxo ligand, C_α and C_β of the neopentylidene ligand, and the chloride ligand all lie in the equatorial plane [W═C(1) = 1.882 (14), W═O = 1.661 (11), and W—Cl(1) = 2.389 (5) Å]. The triethylphosphine ligand and the second chloride ligand occupy the "axial" sites [W—P = 2.518 (4), W—Cl(2) = 2.379 (5) Å]. Although many features of this molecule are worth some discussion we want to comment on only two of them here. The first is the W═C(1) bond length; it is intermediate between the tungsten-alkylidene and tungsten-alkylidyne bond lengths found in $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$ [W═C = 1.942 (9), W≡C = 1.785 (8) Å].[14] The second is the W═C(1)—C(2) angle [140.6 (11)°]; it is the *smallest* of any observed so far in several neopentylidene complexes of Ta[4c,15,16] and W.[14]

We conclude from these studies that alkylidene ligand conformations are more "normal" in electron-deficient[17] Ta or W complexes which contain "hard" alkoxide[18] or oxo ligands, respectively. These complexes are metathesis catalysts.[3] When only "softer" ligands are present (η^5-C_5R_5, Cl, Br, PR_3)[19] and/or when such Ta-alkylidene complexes are formally reduced by two electrons,[20] the alkylidene ligand is distorted such that the M—C_α—C_β angle is 160-170°. These "reduced" alkylidene complexes do not metathesize olefins.[3,19] We have shown[2a,10,21] that, in these cases, the initial metallacyclobutane complex rearranges to an olefin complex too rapidly relative to the rate at which it cleaves to form a new alkylidene complex.

Acknowledgments. We thank the National Science Foundation for support (Grant CHE 77-04981 to M.R.C. and CHE79-05307 to R.R.S.).

References and Notes

(1) Multiple Metal-Carbon Bonds. 16. Part 15: ref 4b.

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(4) (a) We have prepared many octahedral neopentylidene and benzylidene complexes. In all cases to date, all evidence[4b] (including structural studies[4c]) suggests that alkylidene ligands are bound to the metal through at least a double bond and that they lie along one of the axes in the octahedron. (b) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.,* in press. (c) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *Ibid.* **1979,** *101,* 1593–1595.

(5) The stereochemistry is based on the fact that the phosphine ligands are equivalent and that the protons on the methylene ligand (which must lie along an axis[4]) are not equivalent. Since the oxo ligand donates its π electrons to the metal so efficiently it uses two of the three available π-type metal d orbitals. For the third π-type metal d orbital to overlap with the alkylidene α-carbon's $2p_z$ orbital, the CHR ligand must lie in the O-W-C plane.

(6) A typical catalyst system consists of 0.25 mmol of W, 0.25 mmol of nonane, 5 mL of solvent, 20–100 equiv of olefin (as needed), and 0.5 equiv of $AlCl_3$. Only a fraction of the $AlCl_3$ actually dissolves. We add 0.5 equiv simply because small amounts cannot be weighed out as easily and accurately. The reaction is slower if only traces of $AlCl_3$ are added and slows down if greater than ~1 equiv is added. The latter may be due either to precipitation of W-containing solids or to faster catalyst deactivation.

(7) Most Nb- and Ta-alkylidene complexes studies so far give β-elimination products,[2a] the exception being complexes containing alkoxide ligands.[3]

(8) The signal for H_α of **1d** is found at δ 12.10.[3] The signals for the two inequivalent methylene protons in **1e** are found at δ 12.34 and δ 11.47.[3] The ratio of **1d** to **1e** is variable since **1e** is not so stable as the others and since the rate of reaction with 1-butene varies considerably depending on how much is allowed to dissolve. In our case we let the reaction volume increase by ~20% with dissolved 1-butene before isolating the reaction vessel from the 1-butene source.

(9) (a) It has been known for some time in "classical" metathesis systems that the rate of degenerate metathesis via α,α'-disubstituted metallacyclobutane complexes of type **2** is faster than the rate of productive metathesis via complexes of type **3**,[9b] (b) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979,** *17,* 449–492, and references therein.

(10) Rupprecht, G. A.; Rocklage, S.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R., manuscript in preparation.

(11) $W(O)(CHCMe_3)(PEt_3)_2Br_2$ can be prepared in a manner analogous to that for preparing **1a**[3] from $Ta(CHCMe_3)(PEt_3)_2Br_3$[4b] and $W(O)(OCMe_3)_4$ in pentane.

(12) **4** crystallizes preferentially on addition of pentane to the toluene solution. Calcd for $WC_{11}H_{25}OCl_2P$: C, 28.78; H, 5.49. Found: C, 29.08; H, 5.59. ^1H NMR (ppm, C_6D_6): 9.80 (d, 1, $^3J_{PH} = 3$ Hz, H_α), 1.50 (poor q, 6, PCH_2CH_3), 1.13 (s, 9, Me), 0.65 (dt, 9, $^2J_{PH} = 16$ Hz, PCH_2CH_3). ^{13}C NMR (ppm, C_6D_6, gated ^1H decoupled): 295.4 (d, $J_{CH} = 115$ Hz, C_α), 45.4 (s, C_β), 31.2 (q, $J_{CH} = 125$ Hz, CMe_3), 17.4 (t, $J_{CH} = 130$ Hz, PCH_2CH_3), 8.05 (q, $J_{CH} = 129$ Hz, PCH_2CH_3); $J_{C\alpha W} = 176$ Hz in the $^{13}C[^1H]$ NMR spectrum. ^{31}P NMR (ppm, C_6D_6, ^1H decoupled): 40.9 ($J_{PW} = 364$ Hz). Mol wt: calcd, 459; found, 436.

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(17) By electron deficient we mean containing less than 18 valence electrons.

(18) The values for $^1J_{CH\alpha}$ in $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ complexes[3] (M = Nb or Ta) is ~125 Hz. Since $^1J_{CH\alpha}$ inversely correlates in known Ta structures with the M—C_α—C_β angle we assume the angle in the $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ complexes is also on the order of 140–150°.

(19) See ref 2a and references therein.

(20) (a) An example is $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$,[20b] a neutron diffraction study of which[20c] shows that the Ta═C_α—C_β angle is 170.2 (2) and the Ta═C_α—H_α angle is 78.1 (3)°, the C_α—H_α bond length is 1.135 (5) and the Ta═C_α bond length is 1.946 (3) Å, and H_α is only 2.042 (5) Å from Ta. (b) Wood, C. D., unpublished results. (c) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R., submitted for publication.

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(22) Camille and Henry Dreyfus Teacher–Scholar Grant awardee, 1978.

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Intermolecular Reactions of 4,4-Dimethylcyclohex-2-enylidene[1]

Sir:

In an important paper describing intramolecular insertion reactions of alkylcarbenes, Chang and Shechter[3] made the suggestion that excited singlet carbenes could be responsible for much of the chemistry occurring on direct irradiation of

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